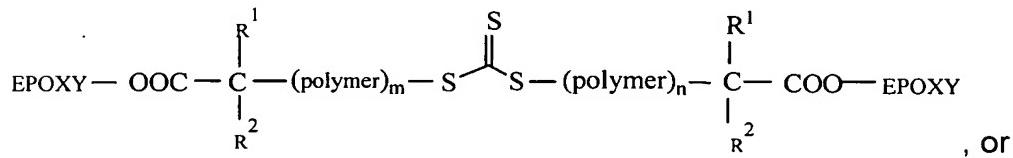


**WHAT IS CLAIMED IS:**

1. A vinyl ester toughener, comprising:  
 the reaction product of a toughener polymer or copolymer and an  
 5 unsaturated monocarboxylic acid;  
 said unsaturated acid being a monoacid containing from 3 to about 10  
 carbon atoms;  
 said toughener polymer having the formula

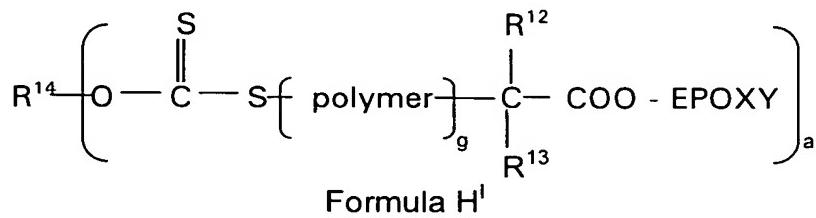
10                                  Formula X<sup>I</sup>

wherein R<sup>1</sup> and R<sup>2</sup>, independently, are an alkyl having 1 to about 6 carbon atoms, an alkyl having from 1 to 6 carbons atoms and 1 or more substituents, at least one aryl, or at least one substituted aryl having from 1 to about 6 substituents on the aryl ring, and wherein said one or more substituents,

15 independently, comprises an alkyl having from 1 to 6 carbon atoms, or an aryl, or a halogen group, or a cyano group, or an ether having a total of from 2 to about 20 carbon atoms, or a nitro group, or combinations thereof,

wherein m and n, independently, is a repeat unit of from about 5 to about 1,000; or

20                                  said toughener polymer or copolymer having the formula:



wherein R<sup>12</sup> and R<sup>13</sup>, independently, can be the same or different, can be a linear or branched alkyl having from 1 to about 12 carbon atoms; or an aryl group having from 6 to about 18 carbon atoms, optionally containing

heteroatoms; or R<sup>12</sup> and R<sup>13</sup> can form or be a part of a substituted or unsubstituted cyclic ring having from 3 to about 12 carbon atoms;

wherein R<sup>14</sup> is optionally substituted, and can be a linear or branched alkyl having from 1 to about 12 carbon atoms, an aryl group optionally

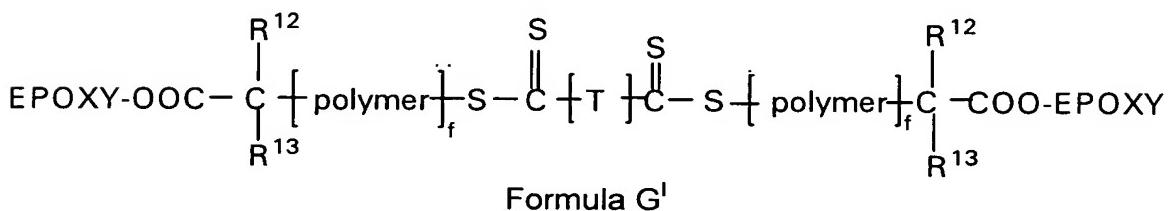
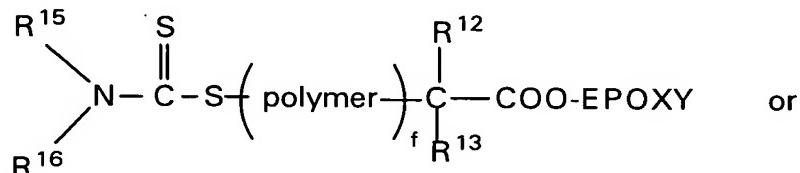
- 5 saturated or unsaturated; an arylalkyl having from about 7 to about 18 carbon atoms; an acyl group; an alkene group; an alkenealkyl having from 3 to about 18 carbon atoms; an alkylene group; an alkoxyalkyl; derived from a polyalkylene glycol; derived from a polyalkylene glycol monoalkyl ether having from about 3 to about 200 carbon atoms; derived from a
- 10 polyalkylene glycol monoaryl ether having from about 3 to about 200 carbon atoms, a polyfluoroalkyl; a phosphorous containing alkyl; or a substituted or unsubstituted aryl ring containing heteroatoms;

wherein said (polymer) is derived from at least one conjugated diene monomer, or a vinyl containing monomer or combinations thereof, with the proviso that each polymer repeat unit can be the same or different;

wherein said g is from about 1 to about 10,000; and

wherein said "a" is 1 to about 4; or

said toughener polymer or copolymer being a dithiocarbamate having the formula:



- 25 wherein each R<sup>12</sup> and R<sup>13</sup>, independently, is the same or different, is optionally substituted, and is a linear or branched alkyl having from 1 to

about 12 carbon atoms; or an aryl group having from 6 to about 18 carbon atoms, optionally containing heteroatoms; or R<sup>12</sup> and R<sup>13</sup> can form and be part of a substituted or unsubstituted cyclic ring having from 3 to about 12 carbon atoms;

5       wherein R<sup>15</sup> and R<sup>16</sup>, independently, is the same or different, optionally substituted, optionally contains heteroatoms, and is hydrogen; or a linear or branched alkyl having from 1 to about 18 carbons; or an aryl group having from 6 to about 18 carbon atoms, optionally saturated or unsaturated; or an arylalkyl having from 7 to about 18 carbons; or an alkenealkyl having from 3  
10      to about 18 carbon atoms; or derived from polyalkylene glycol ether; or derived from an amine; or R<sup>15</sup> and R<sup>16</sup> are in the form of a substituted or unsubstituted cyclic ring with the nitrogen atom having a total of 4 to about 12 carbon atoms;

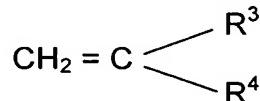
15      wherein T is a divalent radical having a nitrogen atom directly connected to each carbon atom of the two thiocarbonyl groups;

      wherein said (polymer) repeat units are derived from at least one conjugated diene monomer, or a vinyl containing monomer, or combinations thereof, with the proviso that each repeat unit can be the same or different; and

20      wherein the number of said repeat units f, independently, is from 1 to about 10,000.

2. A vinyl ester toughener according to claim 1, wherein said Formula X' (polymer), independently, comprises a polyacrylate or polymethacrylate derived from an alkyl acrylate or alkyl methacrylate monomer wherein said alkyl has from 1 to about 18 carbon atoms, a polymer derived from a vinyl substituted aromatic monomer containing from 8 to about 12 carbon atoms, a polymer derived from a conjugated diene monomer containing from 4 to about 12 carbon atoms, a polymer derived from acrylonitrile, or  
25      combinations thereof, or  
30

wherein said Formula H' conjugated diene monomer has from 4 to 12 carbon atoms, and wherein said vinyl containing monomer has the formula:



wherein R<sup>3</sup> comprises hydrogen, halogen, C<sub>1</sub> – C<sub>4</sub> alkyl, or substituted C<sub>1</sub> - C<sub>4</sub> alkyl wherein said substituents, independently, comprise one or more hydroxy, alkoxy, aryloxy(OR<sup>5</sup>), carboxy, acyloxy, 10 aroyloxy(O<sub>2</sub>CR<sup>5</sup>), alkoxy-carbonyl(CO<sub>2</sub>R<sup>5</sup>), or aryloxy-carbonyl; N-pyrrolidonyl; wherein R<sup>4</sup> comprises hydrogen, R<sup>5</sup>, CO<sub>2</sub>H, CO<sub>2</sub>R<sup>5</sup>, COR<sup>5</sup>, CN, CONH<sub>2</sub>, CONHR<sup>5</sup>, O<sub>2</sub>CR<sup>5</sup>, OR<sup>5</sup> or halogen; and

wherein R<sup>5</sup> comprises C<sub>1</sub> – C<sub>18</sub> alkyl, substituted C<sub>1</sub> – C<sub>18</sub> alkyl, C<sub>2</sub> – C<sub>18</sub> alkenyl, aryl, heterocyclyl, aralkyl, or alkaryl, and wherein said substituents, independently, comprise one or more epoxy, hydroxy, alkoxy, acyl, acyloxy, carboxy, (and salts), sulfonic acid (and salts), alkoxy- or aryloxy-carbonyl, dicyanato, cyano, silyl, halo or dialkylamino, and

wherein g is from about 3 to about 5,000; or

wherein in said Formula F' and G' toughener polymer or copolymer f is 20 from about 3 to about 5,000;

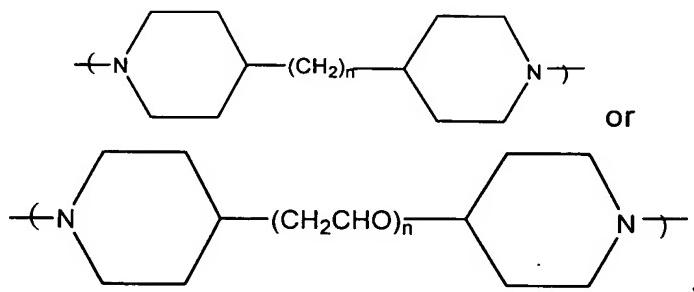
wherein T is:



wherein R<sup>17</sup> and R<sup>18</sup>, independently, is the same or different, is 25 optionally substituted, and is hydrogen; or a linear or branched alkyl having from 1 to about 18 carbon atoms; or an aryl group having from about 6 to about 18 carbon atoms; or an arylalkyl having from 7 to about 18 carbon atoms; or a alkenealkyl having from 3 to about 18 carbon atoms; wherein R<sup>19</sup> is optionally substituted, or is non-existent; or an alkylene group having

from 1 to about 18 carbon atoms; or derived from a polyalkylene glycol either having from 3 to about 200 carbon atoms; wherein R<sup>20</sup> and R<sup>21</sup>, independently, is the same or different, and is optionally substituted, and is an alkylene group having from 1 to about 4 carbon atoms, or

5 wherein T is:



wherein n is 0 to about 18.

- 10 3. A vinyl ester toughener according to claim 2, wherein each said EPOXY, independently, is derived from a: polyhydric phenol polyether alcohol; glycidyl ether of a novolac resin; phenolic novolac epoxy, tetraphenylolethane epoxy, glycidyl ether of mononuclear di- and trihydric phenol; glycidyl ether of bisphenol; glycidyl ether of polynuclear phenol; epoxy resin derived from diphenolic acid; glycidyl ether of aliphatic polyol; glycidyl ester; glycidyl epoxy containing nitrogen; glycidyl derivative of cyanuric acid; glycidyl resin derived from melamine; glycidyl amine; thioglycidyl resin; silicon-glycidyl resin; fluorine glycidyl resin; epoxy resin which is synthesized from monoepoxy other than epihalohydrin including an epoxy resin derived from unsaturated monoepoxy; 15 epoxy resin derived from monoepoxy alcohol; epoxy resin derived from monoepoxy by ester interchange; epoxy resin derived from glyceraldehyde; polyglycidyl compound containing unsaturation; epoxy resin which is synthesized from olefin and chloroacetyl; or an epoxy-resin adduct of the above, or 20 combinations thereof;
- 25 wherein m and n of Formula X<sup>1</sup>, independently, is from about 7 to about 150, and wherein said unsaturated acid is acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, or combinations thereof.

4. A vinyl ester toughener according to claim 3, wherein said Formula X<sup>1</sup> (polymer) is said polyacrylate and said polyacrylate is derived from ethyl acrylate, butyl acrylate, or ethyl-hexyl acrylate, or combinations thereof; wherein R<sup>1</sup> and R<sup>2</sup> are methyl; and

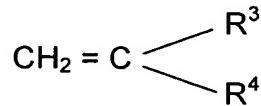
wherein said unsaturated acid is acrylic acid or methacrylic acid; and wherein the amount of said acid is from about 0.85 to about 1.15 mole equivalents based upon the total mole equivalents of said toughener polymer, or

wherein, independently, each said polymer repeat unit of Formula H<sup>1</sup> is derived from alkyl acrylate, vinyl acetate, acrylic acid, styrene, N-vinyl pyrrolidone, or a combination thereof, or

wherein R<sup>12</sup> and R<sup>13</sup>, independently, are an alkyl having from 1 to about 4 carbon atoms, or are part of a cyclic ring, and

wherein "a" is 2, and wherein R<sup>12</sup> and R<sup>13</sup>, independently, are a phenyl group or alkyl group having 1 to about 10 carbon atoms, or R<sup>12</sup> and R<sup>13</sup> are part of a cyclic ring; or

wherein, independently, in Formulas F<sup>1</sup> or G<sup>1</sup>, said conjugated diene monomer has from 4 to 12 carbon atoms, and wherein said vinyl containing monomer has the formula:



wherein R<sup>3</sup> comprises hydrogen, halogen, C<sub>1</sub> – C<sub>4</sub> alkyl, or substituted C<sub>1</sub> - C<sub>4</sub> alkyl wherein said substituents, independently, comprise one or more hydroxy, alkoxy, aryloxy(OR<sup>5</sup>), carboxy, metal carboxylate (COOM) with M being sodium, potassium, calcium, zinc or an ammonium salt, acyloxy, aroyloxy(O<sub>2</sub>CR<sup>5</sup>), alkoxy-carbonyl(CO<sub>2</sub>R<sup>5</sup>), aryloxy-carbonyl; or N-pyrrolidonyl;

30 wherein R<sup>4</sup> comprises hydrogen, R<sup>5</sup>, CO<sub>2</sub>H, CO<sub>2</sub>R<sup>5</sup>, COR<sup>5</sup>, CN, CONH<sub>2</sub>, CONHR<sup>5</sup>, O<sub>2</sub>CR<sup>5</sup>, OR<sup>5</sup> or halogen; and

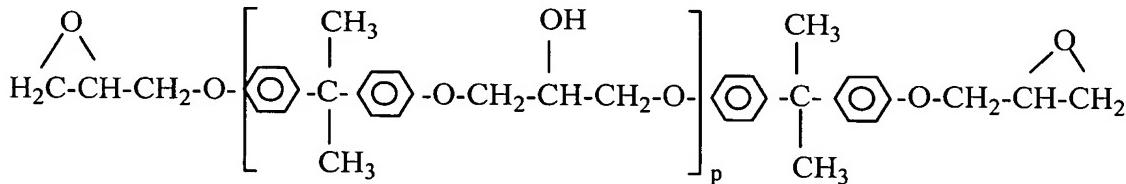
wherein R<sup>5</sup> comprises C<sub>1</sub> – C<sub>18</sub> alkyl, substituted C<sub>1</sub> – C<sub>18</sub> alkyl, C<sub>2</sub> – C<sub>18</sub> alkenyl, aryl, heterocyclyl, aralkyl, or alkaryl, and

wherein said substituents, independently, comprise one or more epoxy, hydroxy, alkoxy, acyl, acyloxy, carboxy, carboxy salts, sulfonic acid,

5 sulfonic salts, alkoxy- or aryloxy-carbonyl, dicyanato, cyano, silyl, halo or dialkylamino.

5. A vinyl ester toughener according to claim 4, wherein in Formula X<sup>I</sup>, m and n, independently, are from about 10 to about 200,

10 wherein each said EPOXY in Formula X<sup>I</sup>, F<sup>I</sup>, G<sup>I</sup>, and H<sup>I</sup>, independently, is derived from



wherein p is from 0.1 to about 1.5, and

wherein the number of said terminal EPOXY groups is from about 1 to  
15 about 2.

6. A vinyl ester toughener according to claim 5, wherein in said Formulas F<sup>I</sup>, G<sup>I</sup>, and H<sup>I</sup> said (polymer) is a polyacrylate, independently, derived from ethyl acrylate, butyl acrylate, or combinations thereof.

20 7. A vinyl ester toughener according to claim 1, including an esterification catalyst, and wherein said reaction occurs at a temperature of from about 90°C to about 150°C.

25 8. A vinyl ester toughener according to claim 3, including an esterification catalyst, and wherein said reaction occurs at a temperature of from about 90°C to about 150°C.

9. A vinyl ester toughener according to claim 5, including an esterification catalyst, and

wherein the reaction occurs at a temperature of from about 105°C to about 135°C.

5

10. A blend of vinyl ester resins, comprising:

a vinyl ester toughener of claim 1, and a vinyl ester epoxy,

said vinyl ester epoxy being the reaction product of at least one epoxy resin and a monounsaturated carboxylic acid having from 3 to about 10 carbon atoms.

10

11. A blend of vinyl ester resins, comprising:

a vinyl ester toughener of claim 2, and a vinyl ester epoxy;

said vinyl ester epoxy being the reaction product of at least one epoxy resin and a monounsaturated carboxylic acid having from 3 to about 10 carbon atoms;

15

wherein said epoxy resin is derived from a: polyhydric phenol polyether alcohol; glycidyl ether of a novolac resin; phenolic novolac epoxy, tetraphenylolethane epoxy, glycidyl ether of mononuclear di- and trihydric phenol; glycidyl ether of bisphenol; glycidyl ether of polynuclear phenol; epoxy resin derived from diphenolic acid; glycidyl ether of aliphatic polyol; glycidyl ester; glycidyl epoxy containing nitrogen; glycidyl derivative of cyanuric acid; glycidyl resin derived from melamine; glycidyl amine; thioglycidyl resin; silicon-glycidyl resin; fluorine glycidyl resin; epoxy resin which is synthesized from monoepoxy other than epihalohydrin including an epoxy resin derived from unsaturated monoepoxy; epoxy resin derived from monoepoxy alcohol; epoxy resin derived from monoepoxy by ester interchange; epoxy resin derived from glycidaldehyde; polyglycidyl compound containing unsaturation; epoxy resin which is synthesized from olefin and chloroacetyl; or an epoxy-resin adduct of the above, or combinations thereof;

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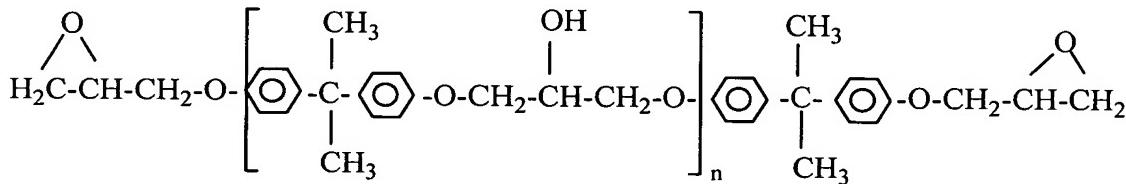
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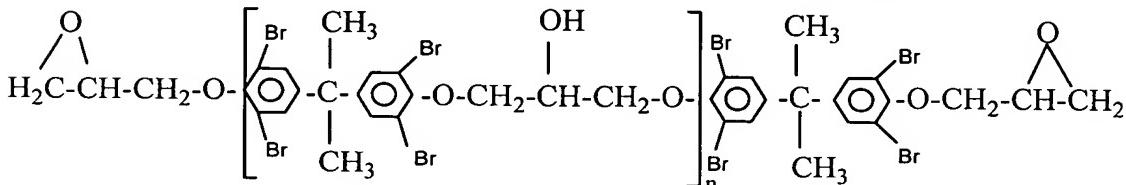
wherein m and n of Formula X<sup>1</sup>, independently, is from about 7 to about 150.

12. A blend of vinyl ester resins, comprising:

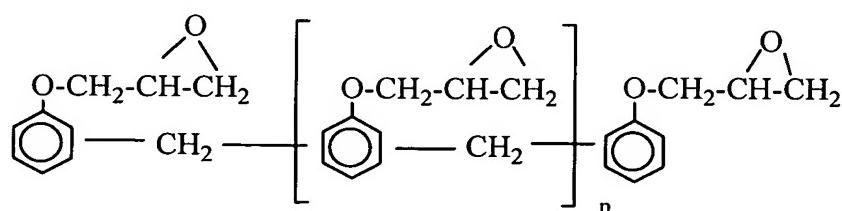
- 5        a vinyl ester toughener of claim 4, and a vinyl ester epoxy;  
       said vinyl ester epoxy being the reaction product of at least one epoxy resin and a monounsaturated carboxylic acid wherein said monounsaturated carboxylic acid is acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, or combinations thereof;
- 10      wherein the amount of said vinyl ester toughener is from about 1 to about 20 parts by weight per 100 parts by weight of said vinyl ester epoxy;  
       and wherein each said epoxy resin, independently, is



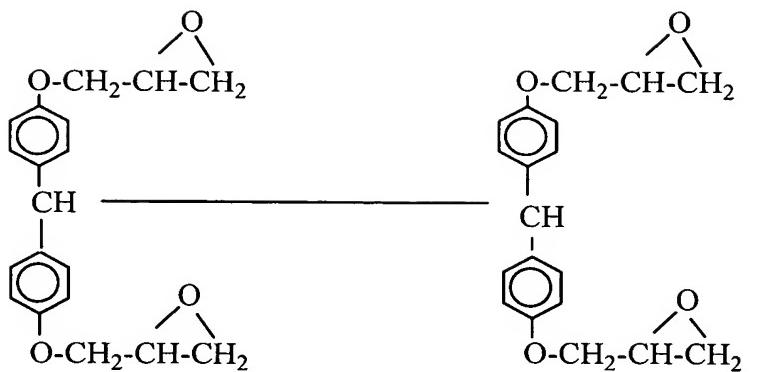
wherein n is an integer from 0 or from about 0.1 to about 18, or;



- 15      wherein n is from 0 or about 0.1 to about 18, or



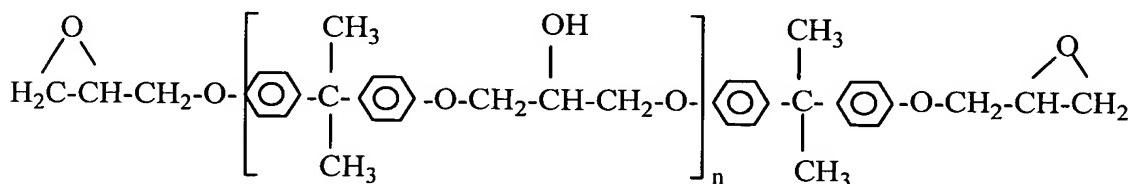
wherein n is from about 0 or about 0.1 to about 8; or



or combinations thereof.

13. A blend of vinyl ester resins, comprising:

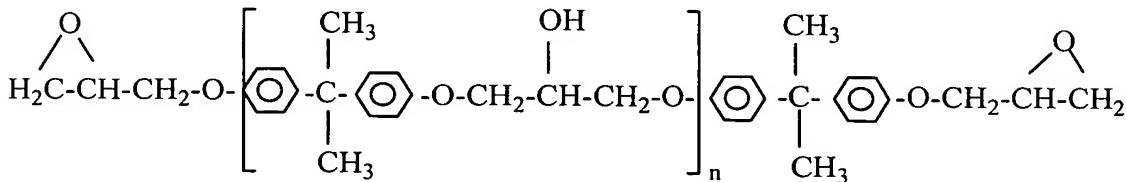
- 5        a vinyl ester toughener of claim 5, and a vinyl ester epoxy;  
       said vinyl ester epoxy being the reaction product of at least one epoxy resin and a monounsaturated carboxylic acid wherein said monounsaturated carboxylic acid is acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, or combinations thereof;
- 10      wherein the amount of said vinyl ester toughener is from about 1 to about 20 parts by weight per 100 parts by weight of said vinyl ester epoxy;  
       and wherein each said epoxy resin, independently, is



wherein n is an integer from 0 or about 0.1 to about 1.5.

- 15      14. A blend of vinyl ester resins, comprising:  
       a vinyl ester toughener of claim 6, and a vinyl ester epoxy;  
       said vinyl ester epoxy being the reaction product of at least one epoxy resin and a monounsaturated carboxylic acid wherein said monounsaturated carboxylic acid is acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, or combinations thereof;

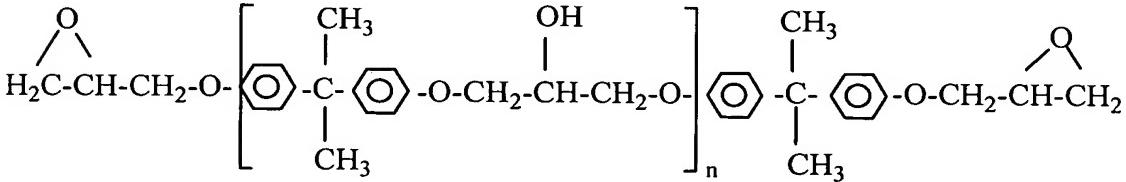
wherein the amount of said vinyl ester toughener is from about 2 to about 15 parts by weight per 100 parts by weight of said vinyl ester epoxy;  
and wherein each said epoxy resin, independently, is



5 wherein n is an integer from 0 or about 0.1 to about 1.5.

15. A blend of vinyl ester resins, comprising:  
a vinyl ester toughener of claim 8, and a vinyl ester epoxy;  
said vinyl ester epoxy being the reaction product of at least one epoxy  
10 resin and a monounsaturated carboxylic acid wherein said monounsaturated carboxylic acid is acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, or combinations thereof;  
wherein the amount of said vinyl ester toughener is from about 2 to about 15 parts by weight per 100 parts by weight of said vinyl ester epoxy;

15 and wherein said each epoxy resin, independently, is



wherein n is an integer from 0 or about 0.1 to about 1.5.

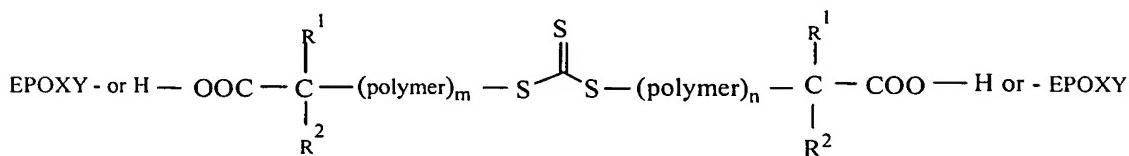
16. The crosslinked composition of claim 10, including a diluent therein,  
20 and optionally including a toughener which is miscible before cure;  
said diluent comprising an unsaturated organic solvent.

17. The crosslinked composition of claim 12, including a diluent, and including a toughener which is miscible before cure;

wherein the amount of said miscible toughener is from about 2 to about 50 parts by weight per 100 parts by weight of said vinyl ester resins

said diluent comprising an unsaturated organic solvent having from 5 to about 15 carbon atoms;

- 5 wherein said miscible toughener has the formula



Formula X<sup>I</sup>

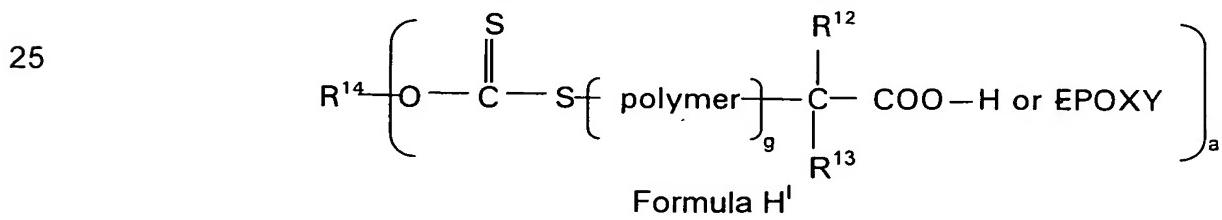
wherein R<sup>1</sup> and R<sup>2</sup>, independently, are an alkyl having 1 to about 6 carbon atoms, an alkyl having from 1 to 6 carbons atoms and 1 or more substituents, at least one aryl, or at least one substituted aryl having from 1 to about 6 substituents on the aryl ring, and wherein said one or more substituents, independently, comprises an alkyl having from 1 to 6 carbon atoms, or an aryl, or a halogen group, or a cyano group, or an ether having a total of from 2 to about 20 carbon atoms, or a nitro group, or combinations thereof,

- 10 15 wherein m and n, independently, is from about 5 to about 1,000,

wherein each said (polymer), independently, comprises a polyacrylate or a polymethacrylate derived from an alkyl acrylate or alkyl methacrylate monomer wherein said alkyl has from 1 to about 18 carbon atoms, a polymer derived from a vinyl substituted aromatic monomer containing from 8 to about 12 carbon

- 20 atoms, a polymer derived from a conjugated diene monomer containing from 4 to about 12 carbon atoms, a polymer derived from acrylonitrile, or combinations thereof; or

a toughener polymer or copolymer having the formula



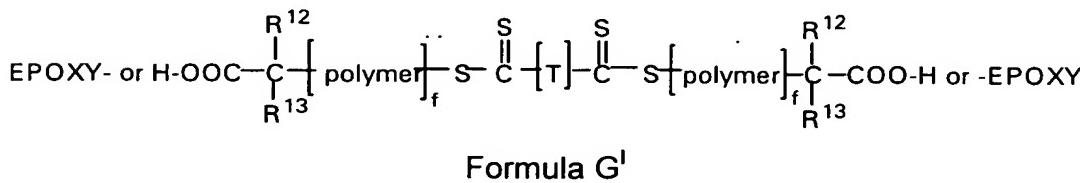
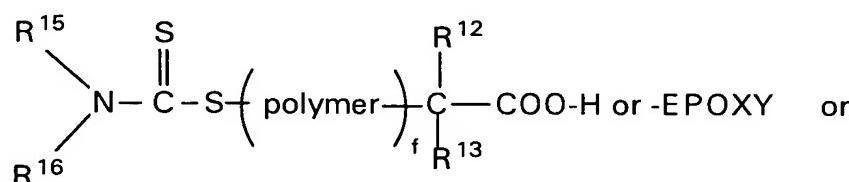
Formula H<sup>I</sup>

wherein R<sup>12</sup> and R<sup>13</sup>, independently, can be the same or different, can be a linear or branched alkyl having from 1 to about 12 carbon atoms; or an aryl group having from 6 to about 18 carbon atoms, optionally containing heteroatoms; or R<sup>12</sup> and R<sup>13</sup> can form or be a part of a substituted or unsubstituted cyclic ring having from 3 to about 12 carbon atoms;

5       wherein R<sup>14</sup> is optionally substituted, and can be a linear or branched alkyl having from 1 to about 12 carbon atoms, an aryl group optionally saturated or unsaturated; an arylalkyl having from about 7 to about 18 carbon atoms; an acyl group; an alkene group; an alkenealkyl having from 3 10      to about 18 carbon atoms; an alkylene group; an alkoxyalkyl; derived from a polyalkylene glycol; derived from a polyalkylene glycol monoalkyl ether having from about 3 to about 200 carbon atoms; derived from a polyalkylene glycol monoaryl ether having from about 3 to about 200 carbon atoms, a polyfluoroalkyl; a phosphorous containing alkyl; or a substituted or 15      unsubstituted aryl ring containing heteroatoms;

wherein the (polymer) is derived from at least one conjugated diene monomer, or a vinyl containing monomer or combinations thereof, with the proviso that each polymer repeat unit can be the same or different;

20       wherein said g is from about 1 to about 10,000; and  
wherein said "a" is 1 to about 4; or  
said toughener polymer or copolymer being a dithiocarbamate having the formula:



wherein each R<sup>12</sup> and R<sup>13</sup>, independently, is the same or different, is optionally substituted, and is a linear or branched alkyl having from 1 to about 12 carbon atoms; or an aryl group having from 6 to about 18 carbon atoms, optionally containing heteroatoms; or R<sup>12</sup> and R<sup>13</sup> can form and be

- 5 part of a substituted or unsubstituted cyclic ring having from 3 to about 12 carbon atoms;

wherein R<sup>15</sup> and R<sup>16</sup>, independently, is the same or different, optionally substituted, optionally contains heteroatoms, and is hydrogen; or a linear or branched alkyl having from 1 to about 18 carbons; or an aryl group having

- 10 from 6 to about 18 carbon atoms, optionally saturated or unsaturated; or an arylalkyl having from 7 to about 18 carbons; or an alkenealkyl having from 3 to about 18 carbon atoms; or derived from polyalkylene glycol ether; or derived from an amine; or R<sup>15</sup> and R<sup>16</sup> are in the form of a substituted or unsubstituted cyclic ring with the nitrogen atom having a total of 4 to about
- 15 12 carbon atoms;

wherein T is a divalent radical having a nitrogen atom directly connected to each carbon atom of the two thiocarbonyl groups;

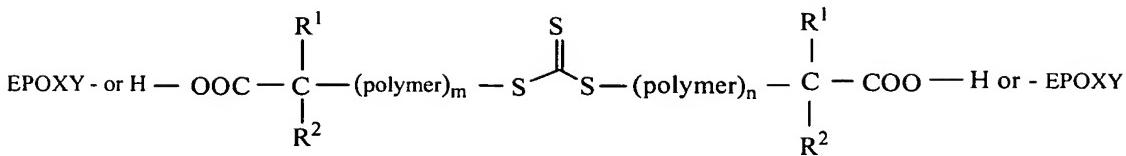
wherein said (polymer) repeat units are derived from at least one conjugated diene monomer, or a vinyl containing monomer, or combinations 20 thereof, with the proviso that each repeat unit can be the same or different; and

wherein the number of said repeat units f, independently, is from 1 to about 10,000.

- 25 18. The crosslinked composition of claim 14, including a diluent therein and including a toughener which is miscible before cure;

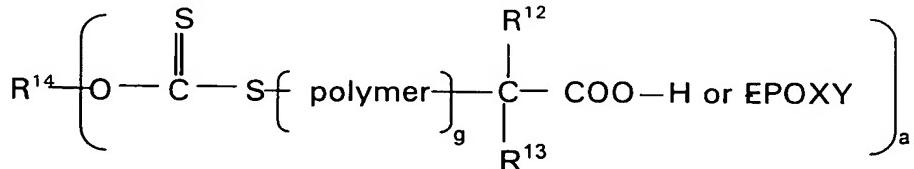
said diluent comprising an unsaturated organic solvent having from 5 to about 15 carbon atoms,

wherein said miscible toughener has the formula

Formula X<sup>I</sup>

wherein R<sup>1</sup> and R<sup>2</sup>, independently, are an alkyl having 1 to about 6 carbon atoms, an alkyl having from 1 to 6 carbons atoms and 1 or more substituents, at least one aryl, or at least one substituted aryl having from 1 to about 6 substituents on the aryl ring, and wherein said one or more substituents, independently, comprises an alkyl having from 1 to 6 carbon atoms, or an aryl, or a halogen group, or a cyano group, or an ether having a total of from 2 to about 20 carbon atoms, or a nitro group, or combinations thereof,

- 5           wherein m and n, independently, is from about 5 to about 500,  
       wherein each said (polymer), independently, comprises a polyacrylate or  
       a polymethacrylate derived from an alkyl acrylate or alkyl methacrylate monomer  
       wherein said alkyl is ethyl, butyl, or combinations thereof; or  
       a toughener polymer or copolymer having the formula

Formula H<sup>I</sup>

15           wherein R<sup>12</sup> and R<sup>13</sup>, independently, can be the same or different, can  
       be a linear or branched alkyl having from 1 to about 12 carbon atoms; or an  
       aryl group having from 6 to about 18 carbon atoms, optionally containing  
       heteroatoms; or R<sup>12</sup> and R<sup>13</sup> can form or be a part of a substituted or  
       unsubstituted cyclic ring having from 3 to about 12 carbon atoms;

- 20           wherein R<sup>14</sup> is optionally substituted, and can be a linear or branched  
       alkyl having from 1 to about 12 carbon atoms, an aryl group optionally  
       saturated or unsaturated; an arylalkyl having from about 7 to about 18  
       carbon atoms; an acyl group; an alkene group; an alkenealkyl having from 3  
       to about 18 carbon atoms; an alkylene group; an alkoxyalkyl; derived from a

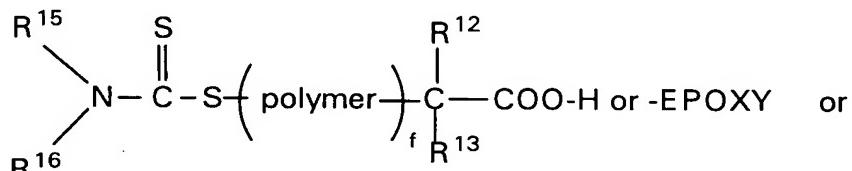
polyalkylene glycol; derived from a polyalkylene glycol monoalkyl ether having from about 3 to about 200 carbon atoms; derived from a polyalkylene glycol monoaryl ether having from about 3 to about 200 carbon atoms, a polyfluoroalkyl; a phosphorous containing alkyl; or a substituted or unsubstituted aryl ring containing heteroatoms;

5 wherein said g is from about 1 to about 10,000; and

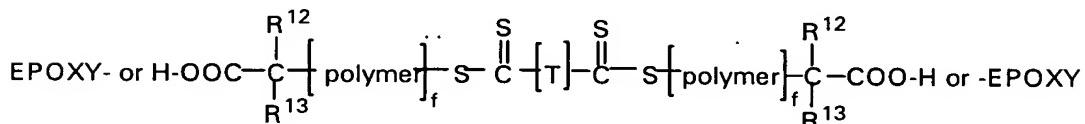
wherein said "a" is 1 to about 4; or

said toughener polymer or copolymer being a dithiocarbamate having the formula:

10



Formula F'



Formula G'

15 wherein each R<sup>12</sup> and R<sup>13</sup>, independently, is the same or different, is optionally substituted, and is a linear or branched alkyl having from 1 to about 12 carbon atoms; or an aryl group having from 6 to about 18 carbon atoms, optionally containing heteroatoms; or R<sup>12</sup> and R<sup>13</sup> can form and be part of a substituted or unsubstituted cyclic ring having from 3 to about 12  
20 carbon atoms;

wherein R<sup>15</sup> and R<sup>16</sup>, independently, is the same or different, optionally substituted, optionally contains heteroatoms, and is hydrogen; or a linear or branched alkyl having from 1 to about 18 carbons; or an aryl group having from 6 to about 18 carbon atoms, optionally saturated or unsaturated; or an arylalkyl having from 7 to about 18 carbons; or an alkenealkyl having from 3 to about 18 carbon atoms; or derived from polyalkylene glycol ether; or

derived from an amine; or R<sup>15</sup> and R<sup>16</sup> are in the form of a substituted or unsubstituted cyclic ring with the nitrogen atom having a total of 4 to about 12 carbon atoms;

5 wherein T is a divalent radical having a nitrogen atom directly connected to each carbon atom of the two thiocarbonyl groups;

wherein the number of said repeat units f, independently, is from 1 to about 10,000;

wherein said (polymer) of said Formulas H<sup>I</sup>, F<sup>I</sup> and G<sup>I</sup>, independently, is a polyacrylate derived from an alkyl acrylate or alkyl methacrylate monomer

10 wherein said alkyl is ethyl acrylate, butyl acrylate, or ethyl-hexyl acrylate, or combinations thereof; and

wherein said EPOXY of said miscible toughener of said Formulas H<sup>I</sup>, F<sup>I</sup> and G<sup>I</sup>, independently, is derived from a: polyhydric phenol polyether alcohol;

glycidyl ether of a novolac resin; phenolic novolac epoxy, tetraphenylolethane epoxy, glycidyl ether of mononuclear di- and trihydric phenol; glycidyl ether of bisphenol; glycidyl ether of polynuclear phenol; epoxy resin derived from diphenolic acid; glycidyl ether of aliphatic polyol; glycidyl ester; glycidyl epoxy containing nitrogen; glycidyl derivative of cyanuric acid; glycidyl resin derived from melamine; glycidyl amine; thioglycidyl resin; silicon-glycidyl resin; fluorine

20 glycidyl resin; epoxy resin which is synthesized from monoepoxy other than epihalohydrin including an epoxy resin derived from unsaturated monoepoxy; epoxy resin derived from monoepoxy alcohol; epoxy resin derived from monoepoxy by ester interchange; epoxy resin derived from glyceraldehyde; polyglycidyl compound containing unsaturation; epoxy resin which is synthesized 25 from olefin and chloroacetyl; or an epoxy-resin adduct of the above, or combinations thereof;

wherein said unsaturated acid is acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, or combinations thereof;

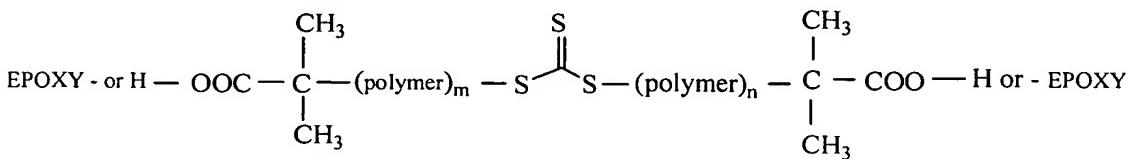
30 wherein the amount of said miscible toughener is from about 2 to about 25 parts by weight per 100 parts by weight of said vinyl ester resins; and

wherein said miscible tougher exists as a discontinuous phase within said crosslinked composition.

19. The crosslinked composition of claim 16, including a diluent therein  
5 and including a toughener which is miscible before cure;

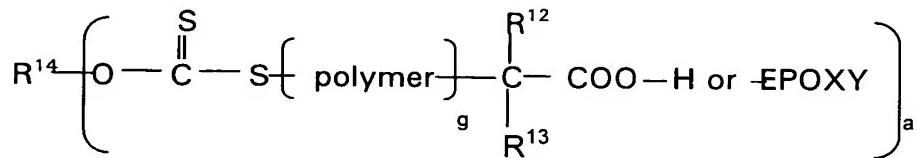
said diluent comprising styrene,  $\alpha$ -methylstyrene, or methacrylate, or an acrylate, or combinations thereof;

wherein said miscible toughener has the formula

10 Formula X<sup>1</sup>

wherein m and n, independently, is from about 5 to about 200,  
wherein each said (polymer), independently, comprises a polyacrylate or a polymethacrylate derived from an alkyl acrylate or alkyl methacrylate monomer wherein said alkyl is ethyl, butyl, or combinations thereof; or

15 a toughener polymer or copolymer having the formula

20 Formula H<sup>1</sup>

wherein R<sup>12</sup> and R<sup>13</sup>, independently, can be the same or different, can be a linear or branched alkyl having from 1 to about 12 carbon atoms; or an aryl group having from 6 to about 18 carbon atoms, optionally containing heteroatoms; or R<sup>12</sup> and R<sup>13</sup> can form or be a part of a substituted or unsubstituted cyclic ring having from 3 to about 12 carbon atoms;

25 wherein R<sup>14</sup> is optionally substituted, and can be a linear or branched alkyl having from 1 to about 12 carbon atoms, an aryl group optionally saturated or unsaturated; an arylalkyl having from about 7 to about 18 carbon atoms; an acyl group; an alkene group; an alkenealkyl having from 3

to about 18 carbon atoms; an alkylene group; an alkoxyalkyl; derived from a polyalkylene glycol; derived from a polyalkylene glycol monoalkyl ether having from about 3 to about 200 carbon atoms; derived from a

5 polyalkylene glycol monoaryl ether having from about 3 to about 200 carbon atoms, a polyfluoroalkyl; a phosphorous containing alkyl; or a substituted or unsubstituted aryl ring containing heteroatoms;

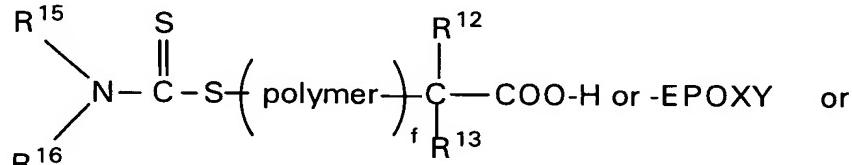
wherein said g is from about 1 to about 10,000; and

wherein said "a" is 1 to about 4;

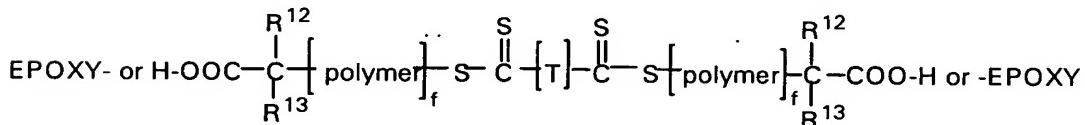
wherein, independently, each said (polymer) repeat unit of Formula H<sup>l</sup> is

10 derived from an alkyl acrylate, vinyl acetate, acrylic acid, styrene, N-vinyl pyrrolidone, or a combination thereof, or

said toughener polymer or copolymer being a dithiocarbamate having the formula:



Formula F<sup>l</sup>



Formula G<sup>l</sup>

wherein each R<sup>12</sup> and R<sup>13</sup>, independently, is the same or different, is

20 optionally substituted, and is a linear or branched alkyl having from 1 to about 12 carbon atoms; or an aryl group having from 6 to about 18 carbon atoms, optionally containing heteroatoms; or R<sup>12</sup> and R<sup>13</sup> can form and be part of a substituted or unsubstituted cyclic ring having from 3 to about 12 carbon atoms;

25 wherein R<sup>15</sup> and R<sup>16</sup>, independently, is the same or different, optionally substituted, optionally contains heteroatoms, and is hydrogen; or a linear or

branched alkyl having from 1 to about 18 carbons; or an aryl group having from 6 to about 18 carbon atoms, optionally saturated or unsaturated; or an arylalkyl having from 7 to about 18 carbons; or an alkenealkyl having from 3 to about 18 carbon atoms; or derived from polyalkylene glycol ether; or

- 5 derived from an amine; or R<sup>15</sup> and R<sup>16</sup> are in the form of a substituted or unsubstituted cyclic ring with the nitrogen atom having a total of 4 to about 12 carbon atoms;

wherein T is a divalent radical having a nitrogen atom directly connected to each carbon atom of the two thiocarbonyl groups;

- 10 wherein the number of said repeat units, independently, is from about 3 to about 5,000;

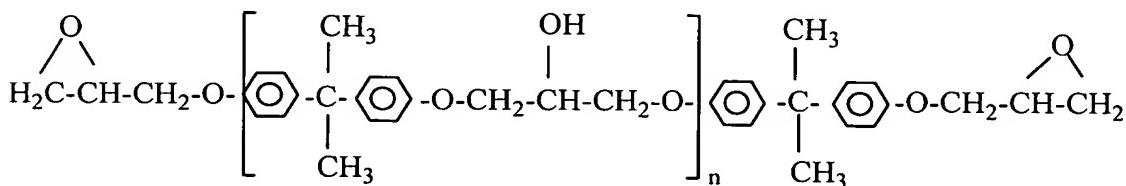
wherein, independently, each said (polymer) repeat unit of Formulas F<sup>1</sup> and G<sup>1</sup> is derived from an alkyl acrylate, vinyl acetate, acrylic acid, styrene, N-vinyl pyrrolidone, or a combination thereof; and

- 15 wherein the amount of said miscible toughener is from about 4 to about 10 parts by weight per 100 parts by weight of said vinyl ester resins;

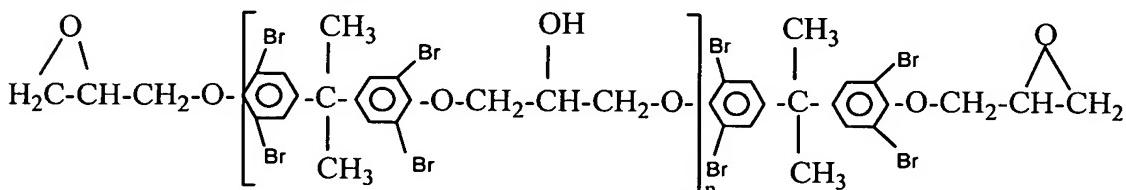
wherein said unsaturated acid is acrylic acid, methacrylic acid, cinnamic acid, crotonic acid, or combinations thereof;

wherein each said EPOXY, independently, of said miscible toughener is

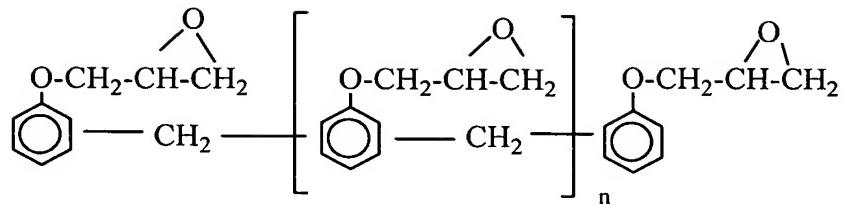
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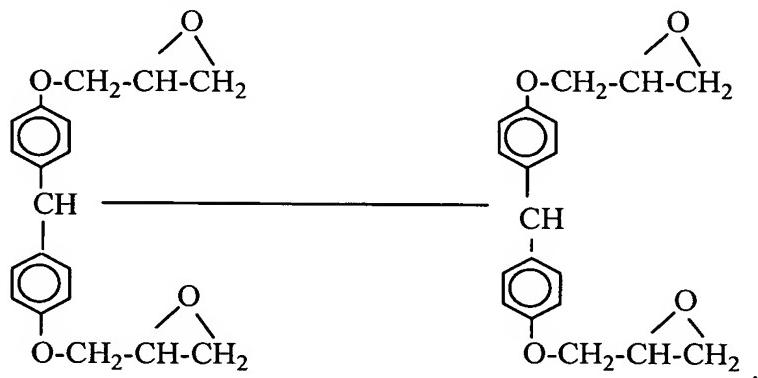
wherein n is an integer from 0 or about 0.1 to about 18, or;



wherein n is from 0 or 0.1 to about 18, or



wherein n is from about 0.0 to about 8; or



or combinations thereof; and

- 5 wherein said miscible toughener exists as a discontinuous phase in said crosslinked composition.

20. The composition of claim 16, which has a shelf stability life of at least two months before cure.

10

21. The composition of claim 17, which has a shelf stability life of at least two months before cure.

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22. The composition of claim 17, which has a shelf stability life of at least four months before cure.

23. The composition of claim 18, which has a shelf stability life of at least four months before cure.

20

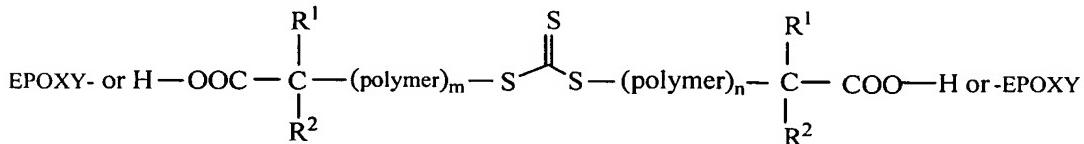
24. The composition of claim 18, which has a self stability life of at least six months before cure.

25. The composition of claim 19, which has a self stability life of at least six months before cure.

5        26. A composition comprising:

a blend of a thermosettable resin and a toughener polymer or copolymer; said thermosettable resin being the reaction product of a polyepoxide having an average of more than one epoxide group per molecule with an unsaturated monocarboxylic acid, or an epoxidized polydiene rubber polymer or 10 copolymer with an unsaturated monocarboxylic acid,

said toughener polymer having the formula



Formula X<sup>I</sup>

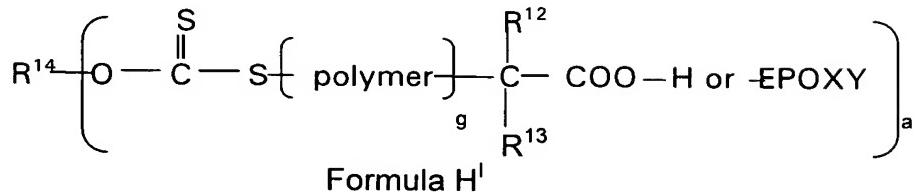
wherein R<sup>1</sup> and R<sup>2</sup>, independently, are an alkyl having 1 to about 6 carbon atoms, an alkyl having from 1 to 6 carbons atoms and 1 or more substituents, at least one aryl, or at least one substituted aryl having from 1 to about 6 substituents on the aryl ring, and wherein said one or more substituents, independently, comprises an alkyl having from 1 to 6 carbon atoms, or an aryl, or a halogen group, or a cyano group, or an ether having a total of from 2 to about 20 carbon atoms, or a nitro group, or combinations thereof,

wherein m and n, independently, is a repeat unit of from about 5 to about 1,000;

wherein each said (polymer), independently, comprises a polyacrylate or polymethacrylate derived from an alkyl acrylate or alkyl methacrylate

monomer wherein said alkyl has from 1 to about 18 carbon atoms, a polymer derived from a vinyl substituted aromatic monomer containing from 8 to about 12 carbon atoms, a polymer derived from a conjugated diene monomer containing from 4 to about 12 carbon atoms, a polymer derived from acrylonitrile, or combinations thereof, or

said toughener polymer having the formula



wherein R<sup>12</sup> and R<sup>13</sup>, independently, can be the same or different, can be a linear or branched alkyl having from 1 to about 12 carbon atoms; or an aryl group having from 6 to about 18 carbon atoms, optionally containing heteroatoms; or R<sup>12</sup> and R<sup>13</sup> can form or be a part of a substituted or unsubstituted cyclic ring having from 3 to about 12 carbon atoms;

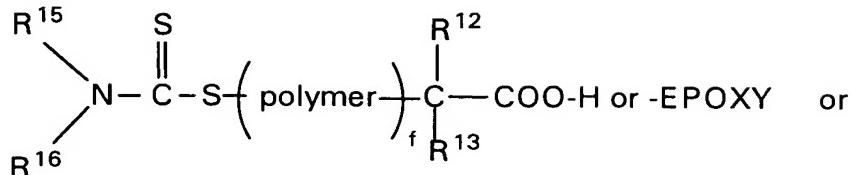
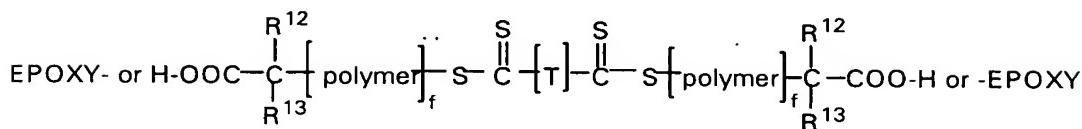
10 wherein R<sup>14</sup> is optionally substituted, and can be a linear or branched alkyl having from 1 to about 12 carbon atoms, an aryl group optionally saturated or unsaturated; an arylalkyl having from about 7 to about 18 carbon atoms; an acyl group; an alkene group; an alkenealkyl having from 3 to about 18 carbon atoms; an alkylene group; an alkoxyalkyl; derived from a polyalkylene glycol; derived from a polyalkylene glycol monoalkyl ether having from about 3 to about 200 carbon atoms; derived from a 15 polyalkylene glycol monoaryl ether having from about 3 to about 200 carbon atoms, a polyfluoroalkyl; a phosphorous containing alkyl; or a substituted or unsubstituted aryl ring containing heteroatoms;

20 wherein said (polymer) is derived from at least one conjugated diene monomer, or a vinyl containing monomer or combinations thereof, with the proviso that each polymer repeat unit can be the same or different;

25 wherein said g is from about 1 to about 10,000; and

wherein said "a" is 1 to about 4; or

said toughener polymer or copolymer being a dithiocarbamate having the formula:

Formula F<sup>1</sup>Formula G<sup>1</sup>

5       wherein each R<sup>12</sup> and R<sup>13</sup>, independently, is the same or different, is  
optionally substituted, and is a linear or branched alkyl having from 1 to  
about 12 carbon atoms; or an aryl group having from 6 to about 18 carbon  
atoms, optionally containing heteroatoms; or R<sup>12</sup> and R<sup>13</sup> can form and be  
part of a substituted or unsubstituted cyclic ring having from 3 to about 12  
10      carbon atoms;

15       wherein R<sup>15</sup> and R<sup>16</sup>, independently, is the same or different, optionally  
substituted, optionally contains heteroatoms, and is hydrogen; or a linear or  
branched alkyl having from 1 to about 18 carbons; or an aryl group having  
from 6 to about 18 carbon atoms, optionally saturated or unsaturated; or an  
arylalkyl having from 7 to about 18 carbons; or an alkenealkyl having from 3  
to about 18 carbon atoms; or derived from polyalkylene glycol ether; or  
derived from an amine; or R<sup>15</sup> and R<sup>16</sup> are in the form of a substituted or  
unsubstituted cyclic ring with the nitrogen atom having a total of 4 to about  
12 carbon atoms;

20       wherein T is a divalent radical having a nitrogen atom directly  
connected to each carbon atom of the two thiocarbonyl groups;

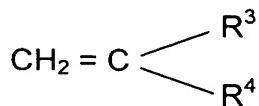
25       wherein said (polymer) repeat units are derived from at least one  
conjugated diene monomer, or a vinyl containing monomer, or combinations  
thereof, with the proviso that each repeat unit can be the same or different;  
and

wherein the number of said repeat units f, independently, is from 1 to about 10,000.

27. A composition according to claim 26,

5        wherein in said thermosettable resin said polydiene rubber polymer is derived from a conjugated diene monomer having from 4 to about 12 carbon atoms, and wherein said polydiene rubber copolymer is derived from a conjugated diene having from 4 to 12 carbon atoms and acrylonitrile,

10      wherein said Formula H<sup>1</sup> conjugated diene monomer has from 4 to 12 carbon atoms, and wherein said vinyl containing monomer has the formula:



15      wherein R<sup>3</sup> comprises hydrogen, halogen, C<sub>1</sub> – C<sub>4</sub> alkyl, or substituted C<sub>1</sub> - C<sub>4</sub> alkyl wherein said substituents, independently, comprise one or more hydroxy, alkoxy, aryloxy(OR<sup>5</sup>), carboxy, acyloxy, aroyloxy(O<sub>2</sub>CR<sup>5</sup>), alkoxy-carbonyl(CO<sub>2</sub>R<sup>5</sup>), or aryloxy-carbonyl; N-pyrrolidonyl;

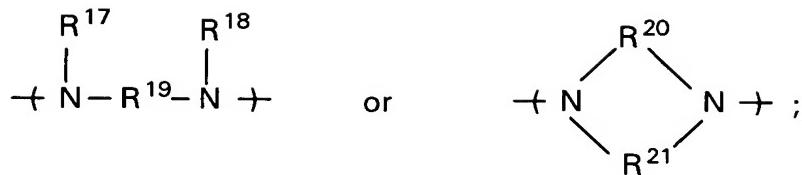
20      wherein R<sup>4</sup> comprises hydrogen, R<sup>5</sup>, CO<sub>2</sub>H, CO<sub>2</sub>R<sup>5</sup>, COR<sup>5</sup>, CN, CONH<sub>2</sub>, CONHR<sup>5</sup>, O<sub>2</sub>CR<sup>5</sup>, OR<sup>5</sup> or halogen; and

25      wherein R<sup>5</sup> comprises C<sub>1</sub> – C<sub>18</sub> alkyl, substituted C<sub>1</sub> – C<sub>18</sub> alkyl, C<sub>2</sub> – C<sub>18</sub> alkenyl, aryl, heterocyclil, aralkyl, or alkaryl, and wherein said substituents, independently, comprise one or more epoxy, hydroxy, alkoxy, acyl, acyloxy, carboxy, (and salts), sulfonic acid (and salts), alkoxy- or aryloxy-carbonyl, dicyanato, cyano, silyl, halo or dialkylamino, and

wherein g is from about 3 to about 5,000; or

wherein in said Formula F<sup>1</sup> and G<sup>1</sup>, toughener polymer or copolymer f is from about 3 to about 5,000;

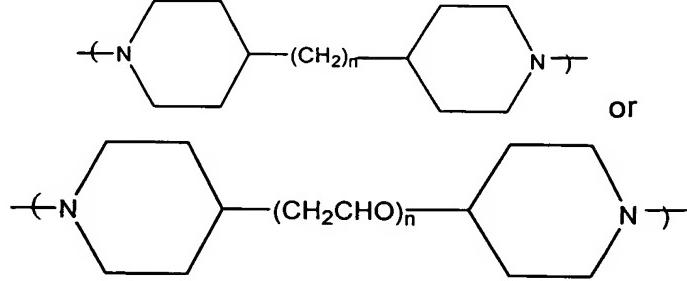
wherein T is:



wherein R<sup>17</sup> and R<sup>18</sup>, independently, is the same or different, is optionally substituted, and is hydrogen; or a linear or branched alkyl having from 1 to about 18 carbon atoms; or an aryl group having from about 6 to

- 5        about 18 carbon atoms; or an arylalkyl having from 7 to about 18 carbon atoms; or a alkenealkyl having from 3 to about 18 carbon atoms; wherein R<sup>19</sup> is optionally substituted, or is non-existent; or an alkylene group having from 1 to about 18 carbon atoms; or derived from a polyalkylene glycol either having from 3 to about 200 carbon atoms; wherein R<sup>20</sup> and R<sup>21</sup>,
- 10      independently, is the same or different, and is optionally substituted, and is an alkylene group having from 1 to about 4 carbon atoms, or

wherein T is:



- 15      wherein n is 0 to about 18.

28.     A composition according to claim 27, wherein in said thermosettable resin said diene rubber polymer or copolymer, independently, is derived from butadiene, isoprene, piperylene, methyl pentadiene, or dimethylhexyladiene, or combinations thereof, and wherein each said monounsaturated acid, independently, is acrylic acid, methacrylic acid, crotonic acid, cinnamic acid or combinations thereof; and

          wherein each said EPOXY, independently, of said toughener is derived from a: polyhydric phenol polyether alcohol; glycidyl ether of a novolac resin;

phenolic novolac epoxy; tetraphenylolethane epoxy; glycidyl ether of mononuclear di- and trihydric phenol; glycidyl ether of bisphenol; glycidyl ether of polynuclear phenol; epoxy resin derived from diphenolic acid; glycidyl ether of aliphatic polyol; glycidyl ester; glycidyl epoxy containing nitrogen; glycidyl

5 derivative of cyanuric acid; glycidyl resin derived from melamine; glycidyl amine; thioglycidyl resin; silicon-glycidyl resin; fluorine glycidyl resin; epoxy resin which is synthesized from monoepoxy other than epihalohydrin including an epoxy resin derived from unsaturated monoepoxy; epoxy resin derived from monoepoxy alcohol; epoxy resin derived from monoepoxy by ester interchange;

10 epoxy resin derived from glycidaldehyde; polyglycidyl compound containing unsaturation; epoxy resin which is synthesized from olefin and chloroacetyl; or an epoxy-resin adduct of the above, or combinations thereof;

and wherein m and n, independently, of Formula X<sup>1</sup> is from about 70 to about 150, and wherein R<sup>1</sup> and R<sup>2</sup> are methyl.

15

29. A composition according to claim 28,

wherein in said thermosettable resin said diene polymer is derived from butadiene and said diene copolymer is derived from butadiene and acrylonitrile, wherein each said unsaturated acid, independently, is acrylic acid or methacrylic acid,

20

wherein each said (polymer), independently, of Formula X<sup>1</sup> is said polyacrylate and said polyacrylate is derived from ethyl acrylate, butyl acrylate, or ethyl-hexyl acrylate, or combinations thereof;

25

wherein, independently, each said polymer repeat unit, independently, of Formula H<sup>1</sup> is derived from alkyl acrylate, vinyl acetate, acrylic acid, styrene, N-vinyl pyrrolidone, or a combination thereof, or

wherein R<sup>12</sup> and R<sup>13</sup>, independently, are an alkyl having from 1 to about 4 carbon atoms, or are part of a cyclic ring, and

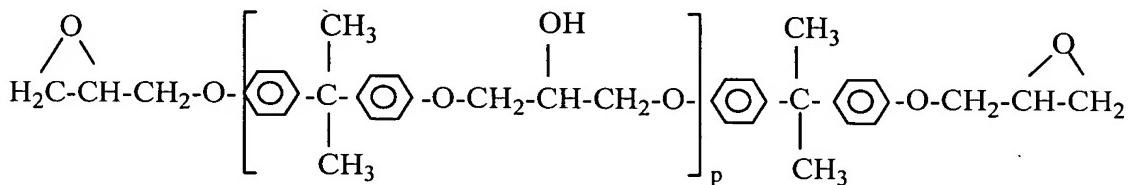
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wherein "a" is 2, and wherein R<sup>12</sup> and R<sup>13</sup>, independently, are a phenyl group or alkyl group having 1 to about 10 carbon atoms, or R<sup>12</sup> and R<sup>13</sup> are part of a cyclic ring; or

wherein, independently, each said polymer of Formulas F<sup>I</sup> or G<sup>I</sup> is derived from an alkyl acrylate, vinyl acetate, acrylic acid, styrene, N-vinyl pyrrolidone, or a combination thereof.

5       30. A composition according to claim 29, wherein said polyepoxy of said thermosettable resin is said glycidyl polyether of a polyhydric alcohol or a polyhydric phenol having an equivalent weight per epoxide group of from about 150 to about 1,500;

10      and wherein each said EPOXY, independently, of said toughener is derived from



wherein p is from 0.1 to about 1.5, and  
wherein the number of said terminal EPOXY groups is from about 1 to about 2.

15      31. A composition according to claim 26, including a diluent, and wherein said diluent is an organic solvent.

20      32. A composition according to claim 28, including a diluent, and wherein said diluent is an organic solvent.

33. A composition according to claim 30, including a diluent, and wherein said diluent is styrene, vinyl toluene, acrylic or methacrylic ester.

25      34. The composition of claim 26, which is crosslinked.

35. The composition of claim 31, which is crosslinked.

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36. The composition of claim 32, which is crosslinked.

37. The composition of claim 33, which is crosslinked.